(54) **Title:** METHOD OF FORMING NON-SAG MOLYBDENUM-LANTHANA ALLOYS

(57) **Abstract:** A method for forming a molybdenum-lanthana alloy is described wherein a non-sag microstructure is achieved by mechanically working an as-sintered or recrystallized body to obtain a degree of deformation of from about 7‰ to about 18‰‰ and then subjecting the lightly worked body to a final recrystallization.

Method of Forming Non-sag Molybdenum-Lanthana Alloys

TECHNICAL FIELD

This invention relates generally to methods for forming dispersion-strengthened alloys of molybdenum. More particularly, this invention relates to methods of forming molybdenum-lanthana alloys having non-sag microstructures.

BACKGROUND OF THE INVENTION

Molybdenum alloys which have been dispersion-strengthened with particles of lanthanum oxide (lanthana), La_2O_3, are desirable for use in high temperature applications because of their high melting point and good mechanical properties at high temperatures, in particular, resistance to sag and creep. The alloys are formed by combining molybdenum powder with from about 0.1 to about 5 weight percent (wt.%) of lanthanum oxide powder or an equivalent amount of a lanthanum oxide precursor, such as $La(OH)_3$ or $La(NO_3)_3$, which is then converted to the oxide by heating. The size of the lanthanum oxide particles dispersed in the molybdenum matrix is generally preferred to be less than about 1 μm, however, the particles may be as large 5-10 μm. After compacting and sintering, the sintered body is deformed by mechanical working, e.g., rolling, swaging, drawing, or hammering, and then is then recrystallized to generate the desired microstructure. For sag and creep resistance, the preferred microstructure consists of large, interlocking grains which are elongated in the direction of the applied mechanical work.

The recrystallization behavior of the alloy is affected by the prior amount of deformation. When the undeformed or fully recrystallized alloy is being cold worked, the density of dislocations within the alloy increases. This occurs first at the grain boundaries and then progresses further into the bulk of the grains as the amount of cold work increases. Prior art methods have employed high degrees of deformation (>60%) in order to achieve high-temperature strength and creep-resistance.

Japanese Patent Publication 59-177345 (1984) describes a molybdenum-lanthana alloy for structural purposes. The alloy has a high secondary recrystallization temperature and high high-temperature strength. The alloy contains 1 to 5 wt.% lanthana (La_2O_3) particles having an average size of not more than 3 μm which are uniformly dispersed in molybdenum. For structural purposes, the material is preferably worked from the sinter by a working factor of at least 60% and then heated above the secondary recrystallization temperature.

U.S. Patent No. 4,950,327 to Eck et al. (1990) describes a high-temperature, creep-resistant molybdenum-lanthana alloy having a tiered structural arrangement. After sintering, the alloy is mechanically reformed in gradations of about 10% without heating the alloy above its recrystallization temperature. Once the degree of reforming is at least 85%, the alloy is finally subjected to a recrystallization anneal.

One disadvantage with the prior art methods is that the dimensions of the feed material must be substantially greater than the dimensions of the finally recrystallized material in order to impart the required high degree of deformation. This

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leads to less flexibility in the manufacturing process. Another disadvantage is that the large amount of stored energy in the material caused by the high degree of deformation can lead to spontaneous grain growth in the material during recrystallization. This may make it more difficult to control grain size in the finally recrystallized material.

SUMMARY OF THE INVENTION

It has been discovered that a non-sag microstructure can be obtained in a molybdenum-lanthana alloy using a degree of deformation of from about 7% to about 18%. As used herein, the degree of deformation refers to the percentage reduction in at least one dimension of the feed material, e.g., sheet thickness. Preferably, the degree of deformation is from about 12% to about 17%. The alloy may be deformed directly from the as-sintered state to its finished form and then finally recrystallized or, preferably, the alloy can worked from the as-sintered state to a near-finished form, recrystallized, and then deformed to its finished form and finally recrystallized. Preferably, the recrystallization of the alloy in its near-finished form is conducted at a temperature of from about 1150°C to about 1400°C. The final recrystallization is preferably conducted at about 1900°C. Preferably, the amount of lanthana in the alloy ranges from 0.4 wt.% to about 1.0 wt.%, more preferably, from about 0.6 wt.% to about 0.7 wt.%.

The grain size after final recrystallization is larger because the predominant mechanism occurring during the heat treatment is the annihilation of dislocations at the neighboring grain boundaries causing some grain boundaries to disappear. This is generally referred to as strain-induced grain boundary migration. After final recrystallization, the grains tend to

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exhibit less elongation than grains resulting from methods which use high degrees of deformation. Typically, the aspect ratio for the grains produced by the method of this invention is no more than 4:1. Also, since the degree of reformation needed to produce the non-sag microstructure is about 18% or less, the feed material need not be much larger than the finished product and there is a greater potential to control grain size in the finished material because of the lower amount of stored energy in the material prior to final recrystallization. Hence, the method of this invention is more flexible for manufacturers of refractory metal products.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a photomicrograph of the microstructure of the molybdenum-lanthana alloy of Example 1 after recrystallization and rolling to 0.15 cm thickness.

Fig. 1B is a photomicrograph of non-sag microstructure of the molybdenum-lanthana alloy of Example 1 after final recrystallization.

Fig. 2A is a photomicrograph of the microstructure of the molybdenum-lanthana alloy of Example 2 after recrystallization and rolling to 0.10 cm thickness.

Fig. 2B is a photomicrograph of non-sag microstructure of the molybdenum-lanthana alloy of Example 2 after final recrystallization.

DETAILED DESCRIPTION OF THE INVENTION

For a better understanding of the present invention, together with other and further objects, advantages and capabilities

thereof, reference is made to the following disclosure and appended claims taken in conjunction with the above-described drawings.

EXAMPLE 1

Pure molybdenum metal powder with grain size of 3.5 μm was mixed with 0.7 weight percent (wt.%) of La(OH)$_3$ powder having a grain size of 0.65 μm. The mixture was isostatically pressed at 240 MPa to form a pressed slab with dimensions of 64 cm x 38 cm x 5 cm. The slab was subsequently rolled at varying temperatures; starting at 980°C, followed by 785°C, and finally at ambient temperature to a thickness of 0.17 cm. The sheet was then recrystallized at 1400°C and then rolled at ambient temperature to the thickness of 0.15 cm, (about 12% deformation). The microstructure of the recrystallized and rolled sheet is shown in Fig. 1A. The rolled sheet was subjected to a final recrystallization anneal at 1900°C to produce the non-sag microstructure which is shown in Fig. 1B.

Example 2

Pure molybdenum metal powder with grain size of 3.5 μm was mixed with 0.7 wt.% La(OH)$_3$ powder with a grain size of 0.65 μm. The mixture was isostatically pressed at 240 MPa to form a pressed slab with dimensions of 64 cm x 38 cm x 5 cm. The slab was subsequently rolled at varying temperatures; starting at 980°C, followed by 785°C, and finally at ambient temperature to a thickness of 0.12 cm. The sheet was then recrystallized at 1150°C. Subsequently it was rolled at ambient temperature to the

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thickness of 0.10 cm (about 17% deformation). The microstructure of the recrystallized and rolled sheet is shown in Fig. 2A. Upon a final recrystallization anneal at 1900°C, the sheet material exhibited the non-sag microstructure shown in Fig. 2B.

The sag resistance of 0.5 in. x 5.6 in. samples of the non-sag molybdenum-lanthana sheet material from Examples 1 and 2 was measured according to the following procedure. The samples were supported at opposite ends and a 10 g weight placed on the sample at the center point between the supports. The distance between the supports was 4.2 inches. At the start of the test, the distance between the reference plate and the 0.15-cm-thick sample was 0.5 in. at the point directly below the 10-g load. The corresponding distance for the 0.10-cm-thick sample was 0.4375 in. at the start of the test. Sag was measured as the amount of deflection of the sample toward the reference plate after heating the sample at 1900°C for 1 hour. Six such heating cycles were carried out for each sample and the amount of deflection measured after each cycle. The cumulative amount of deflection is reported in the following table. The sag resistance of the materials was found to be equivalent to commercially available non-sag molybdenum-lanthana sheet material.

Table

Material Thickness	Width (in.)	Length (in.)	Center Load (g)	Total Sag (in.)
0.15 cm	0.5	5.6	9.99	0.0625
0.10 cm	0.5	5.6	9.98	0.0313

While there has been shown and described what are at the present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

CLAIMS

I claim:

1.   A method for forming a non-sag molybdenum-lanthana alloy comprising:

    (a) forming a sintered body of a molybdenum-lanthana alloy wherein the alloy contains from about 0.1 weight percent to about 5 weight percent lanthana;

    (b) mechanically working the sintered body to a near-finished form;

    (c) recrystallizing the sintered body in its near-finished form;

    (d) mechanically deforming the sintered body to a finished form wherein the degree of deformation is from about 7% to about 18%; and

    (e) subjecting the sintered body in its finished form to a final recrystallization annealing.

2.   The method of claim 1 wherein the degree of deformation is from about 12% to about 17%.

3.   The method of claim 1 wherein the final recrystallization annealing is performed at about 1900°C.

4.   The method of claim 1 wherein the sintered body in its near-finished form is recrystallized at a temperature from about 1150°C to about 1400°C.

5.   The method of claim 1 wherein the molybdenum-lanthana alloy contains from about 0.4 weight percent to about 1.0 weight percent lanthana.

6.   The method of claim 1 wherein the sintered body is subjected to one or more heat treatments during the mechanical working in step (b).

7.   The method of claim 3 wherein the molybdenum-lanthana alloy contains from about 0.6 weight percent to about 0.7 weight percent lanthana.

8.   A method for forming a non-sag molybdenum-lanthana alloy comprising:

    (a) forming a sintered body of a molybdenum-lanthana alloy wherein the alloy contains from about 0.4 weight percent to about 1.0 weight percent lanthana;

    (b) mechanically working the sintered body to a near-finished form;

    (c) recrystallizing the sintered body in its near-finished form at a temperature from about 1150°C to about 1400°C;

    (d) mechanically deforming the sintered body to a finished form wherein the degree of deformation is from about 7% to about 18%; and

    (e) subjecting the sintered body in its finished form to a final recrystallization annealing at a temperature of about 1900°C.

9.   The method of claim 8 wherein the degree of deformation is from about 12% to about 17%.

10.   The method of claim 8 wherein the molybdenum-lanthana alloy contains from about 0.6 weight percent to about 0.7 weight percent lanthana.

11.   A method for forming a non-sag molybdenum-lanthana alloy comprising:

        (a) forming a sintered body of a molybdenum-lanthana alloy wherein the alloy contains from about 0.1 weight percent to about 5 weight percent lanthana;

        (b) mechanically deforming the sintered body to a finished form wherein the degree of deformation is from about 7% to about 18%; and

        (c) subjecting the sintered body in its finished form to a final recrystallization annealing.

12.   The method of claim 11 wherein the degree of deformation is from about 12% to about 17%.

13.   The method of claim 11 wherein the final recrystallization annealing is performed at about 1900°C.
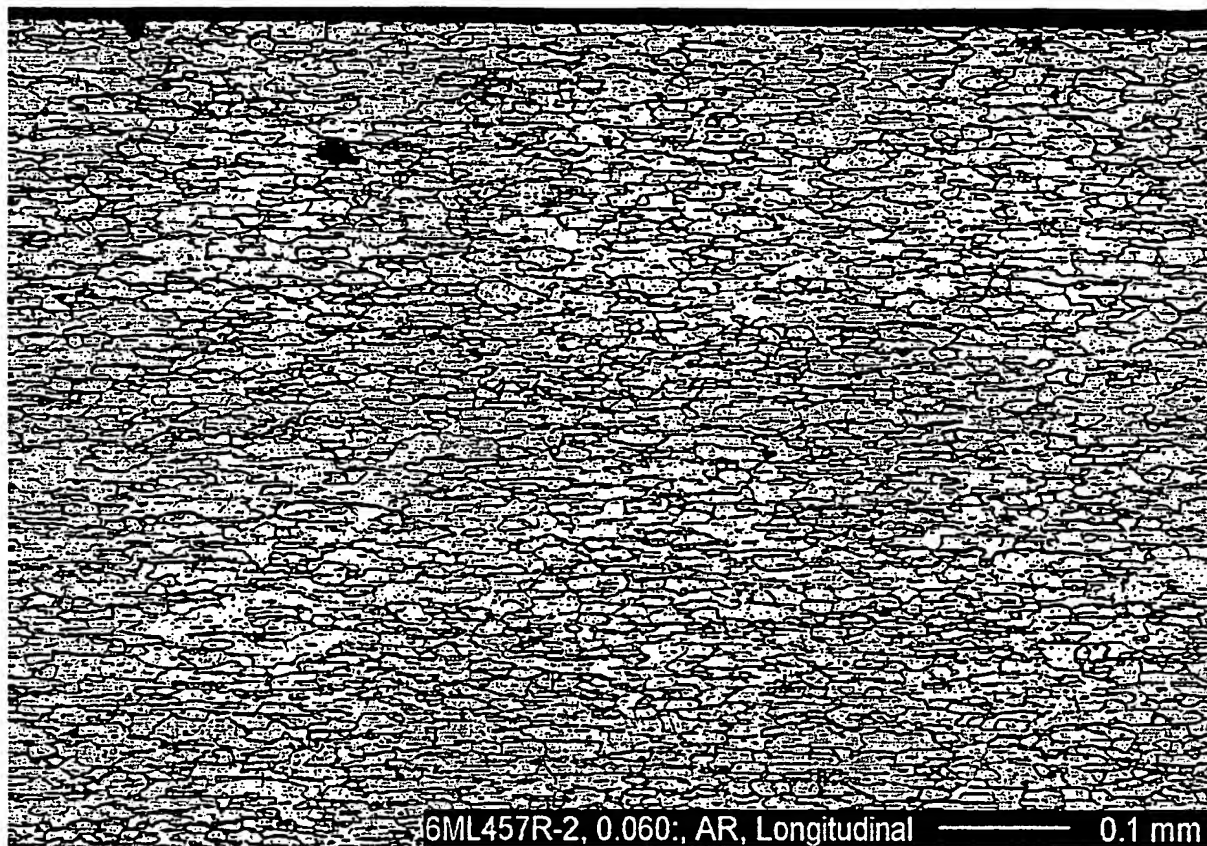
14.   The method of claim 11 wherein the molybdenum-lanthana alloy contains from about 0.4 weight percent to about 1.0 weight percent lanthana.

15.   The method of claim 11 wherein the molybdenum-lanthana alloy contains from about 0.6 weight percent to about 0.7 weight percent lanthana.

16.   The method of claim 13 wherein the degree of deformation is from about 12% to about 17%.
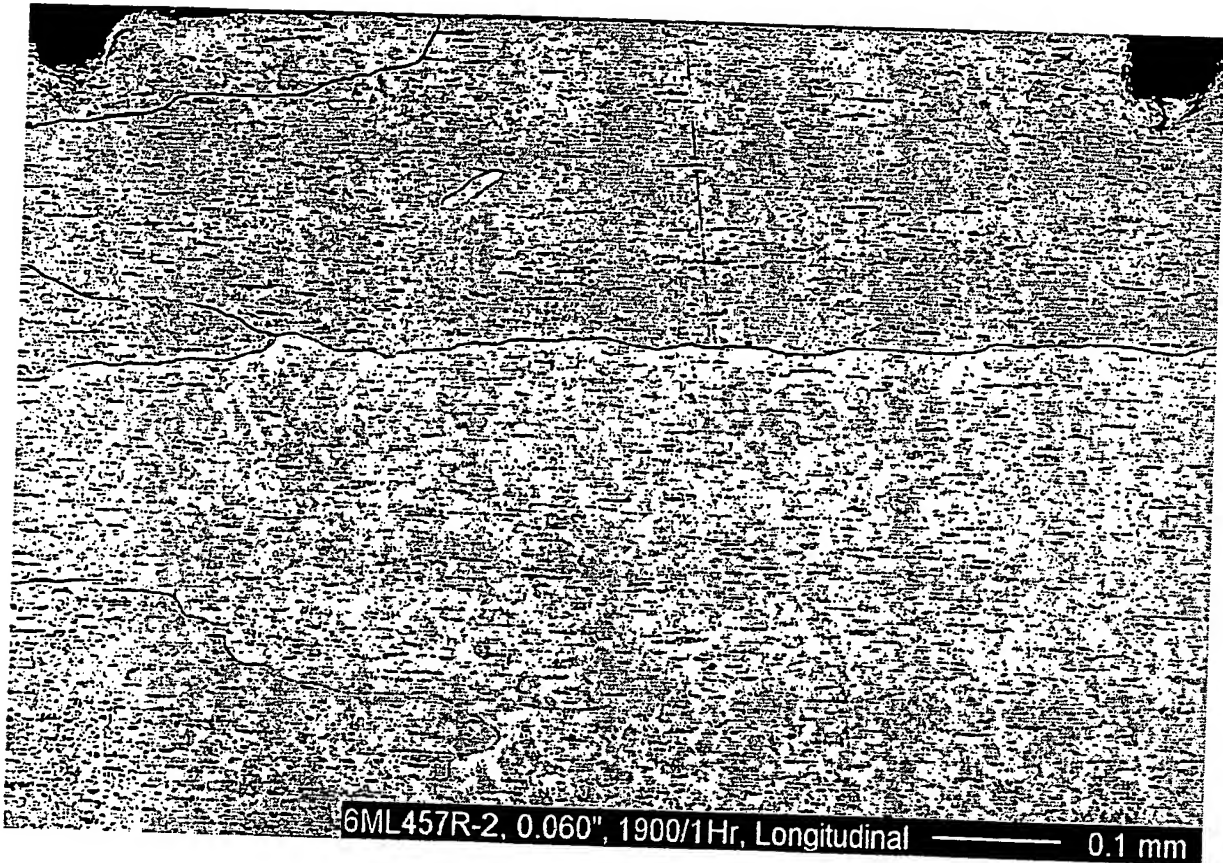
17. The method of claim 16 wherein the molybdenum-lanthana alloy contains from about 0.6 weight percent to about 0.7 weight percent lanthana.

Fig. 1A

6ML457R-2, 0.060:, AR, Longitudinal ——— 0.1 mm
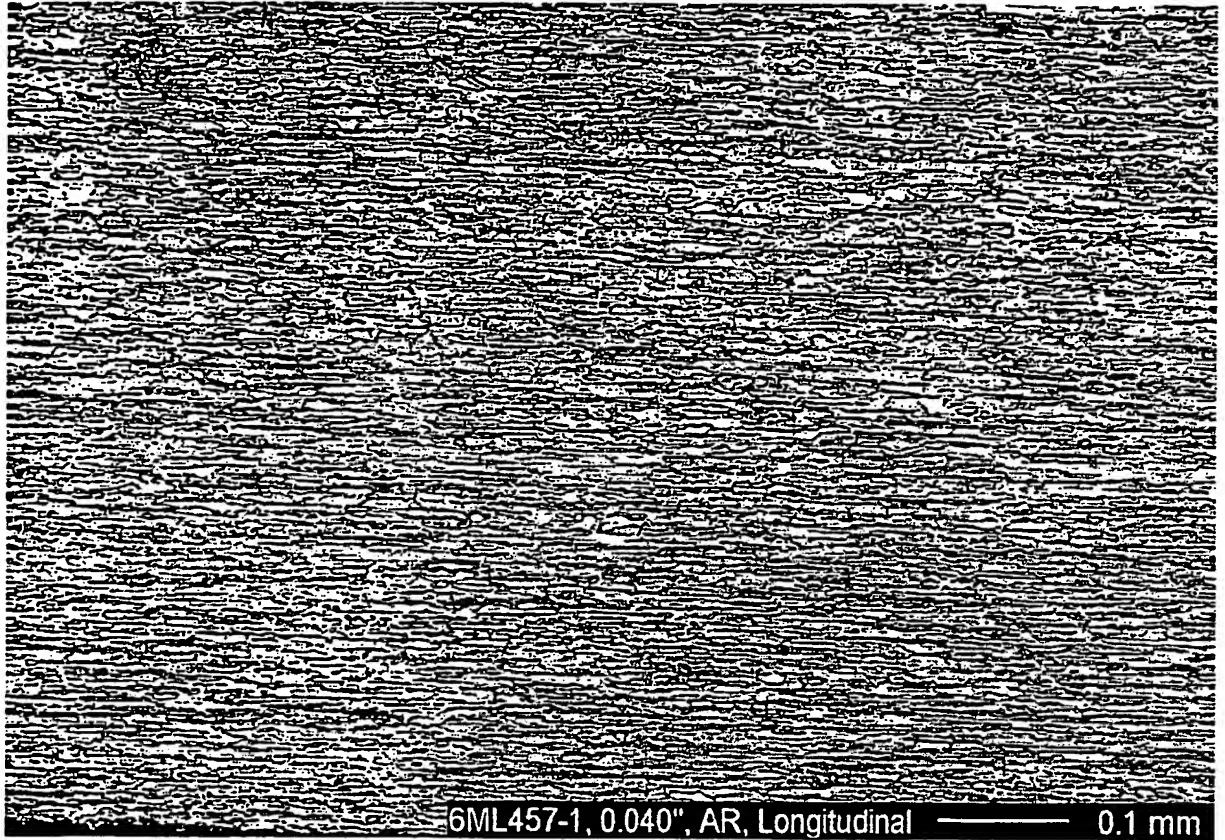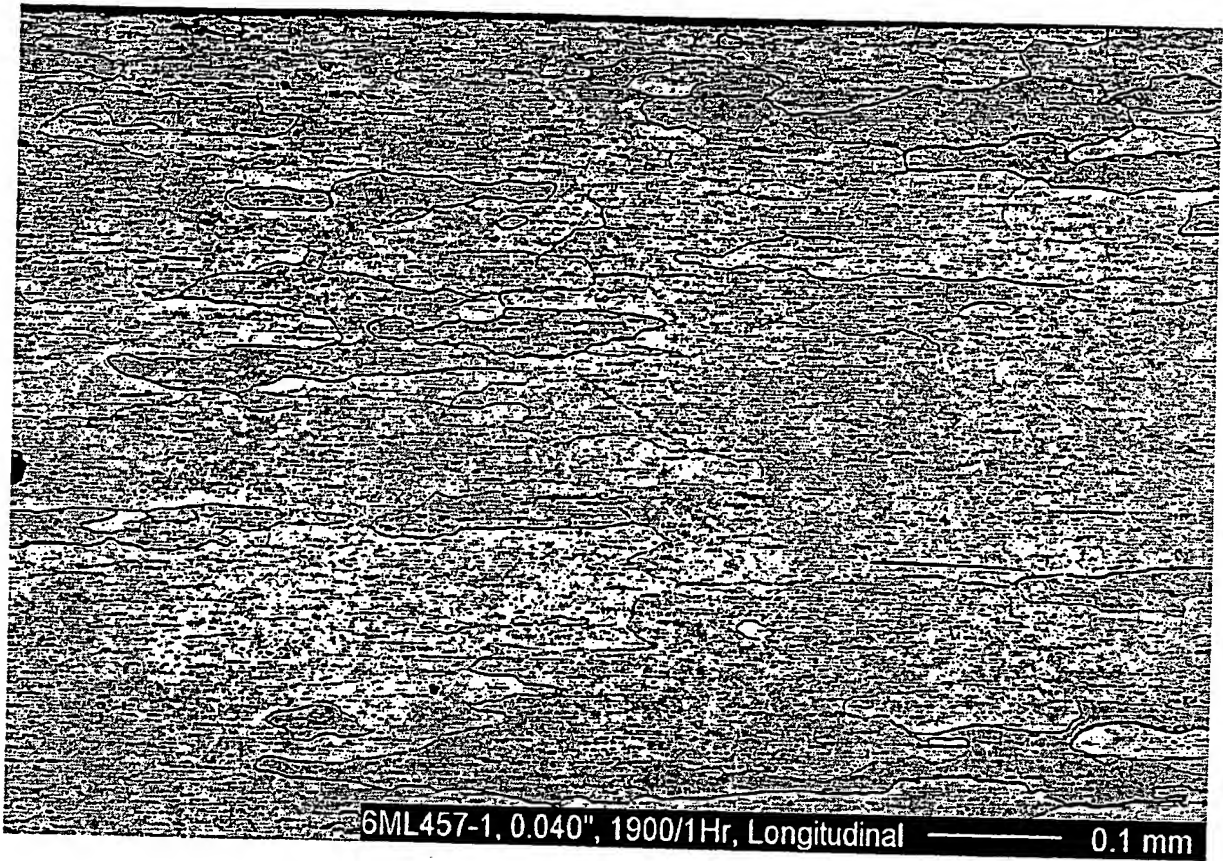
Fig. 1B

6ML457R-2, 0.060", 1900/1Hr, Longitudinal ——————— 0.1 mm

Fig. 2A

6ML457-1, 0.040", AR, Longitudinal ———————— 0.1 mm

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Fig. 2B

6ML457-1, 0.040", 1900/1Hr, Longitudinal ——————— 0.1 mm

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C22C 1/05, 27/04
US CL   :420/429
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 420/429

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST: (molybdenum near alloy) and (lanthana or "lanthanum oxide")

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,785,801 A (BENJAMIN) 15 January 1974.	NONE
A	US 4,950,327 A (ECK et al) 21 August 1990.	
A	US 5,134,039 A (ALEXANDER et al) 28 July 1992.	
A	US 5,435,829 A (FISTER et al) 25 July 1995.	
A	US 5,835,841 A (YAMADA et al) 10 November 1998.	
Y	US 5,868,876 A (BIANCO et al) 9 February 1999, col. 3, line 48 to col. 4, line 39.	1-17
Y	US 6,102,979 A (BIANCO et al) 15 August 2000, col. 3, line 12 to col. 4, line 13.	1-17

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	
"P"	document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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